Phase Equilibria

C:\a-StudioClassroom\minex20.doc; July 7, 2005

	S/mole	V/mole	E/mole
	J/mol-K	cc/mol	J/mol
grossular	255.5	125.3	-6656700
quartz	41.46	22.688	-910700
anorthite	199.3	100.79	-4243040
wollastonite	82.01	39.93	-1635220

Write the formulas for the four (above) minerals.

How many (minimum) chemical components (= C) are needed to describe these compositions. (That is, how many different reagents would you need to mix up all of these compositions.)

Write and balance a reaction that involved grossular, quartz, anorthite and wollastonite. This reaction involves four mineral phase (= P). It plots as a line in P-T space (F = 1).

The volume change of the reaction (= ΔV) is the sum of the volumes of the products minus the sum of the reactants. Calculate the volume change of the reaction. Note: if the reaction involves, for example, 3 moles of quartz, you must multiply the volume of quartz by 3.

The entropy change of the reaction (= ΔS) is the sum of the entropies of the products minus the sum of the reactants. Calculate the entropy change of the reaction. Note: if the reaction involves, for example, 3 moles of quartz, you must multiply the entropy of quartz by 3.

The laws of thermodynamics say that high density assemblages are stable at high pressure, and high entropy assemblages are stable at high temperature.

Which mineral assemblage (which side of the reaction) has highest density and is therefore the high-pressure assemblage?

What about temperature? Which side of the reaction is the high temperature side?

At equilibrium (along the reaction curve)

Gibbs Energy of Reaction =)G = 0

and for a given pressure (P) and temperature (T) we can calculate

)G =)E + P)V - T)S

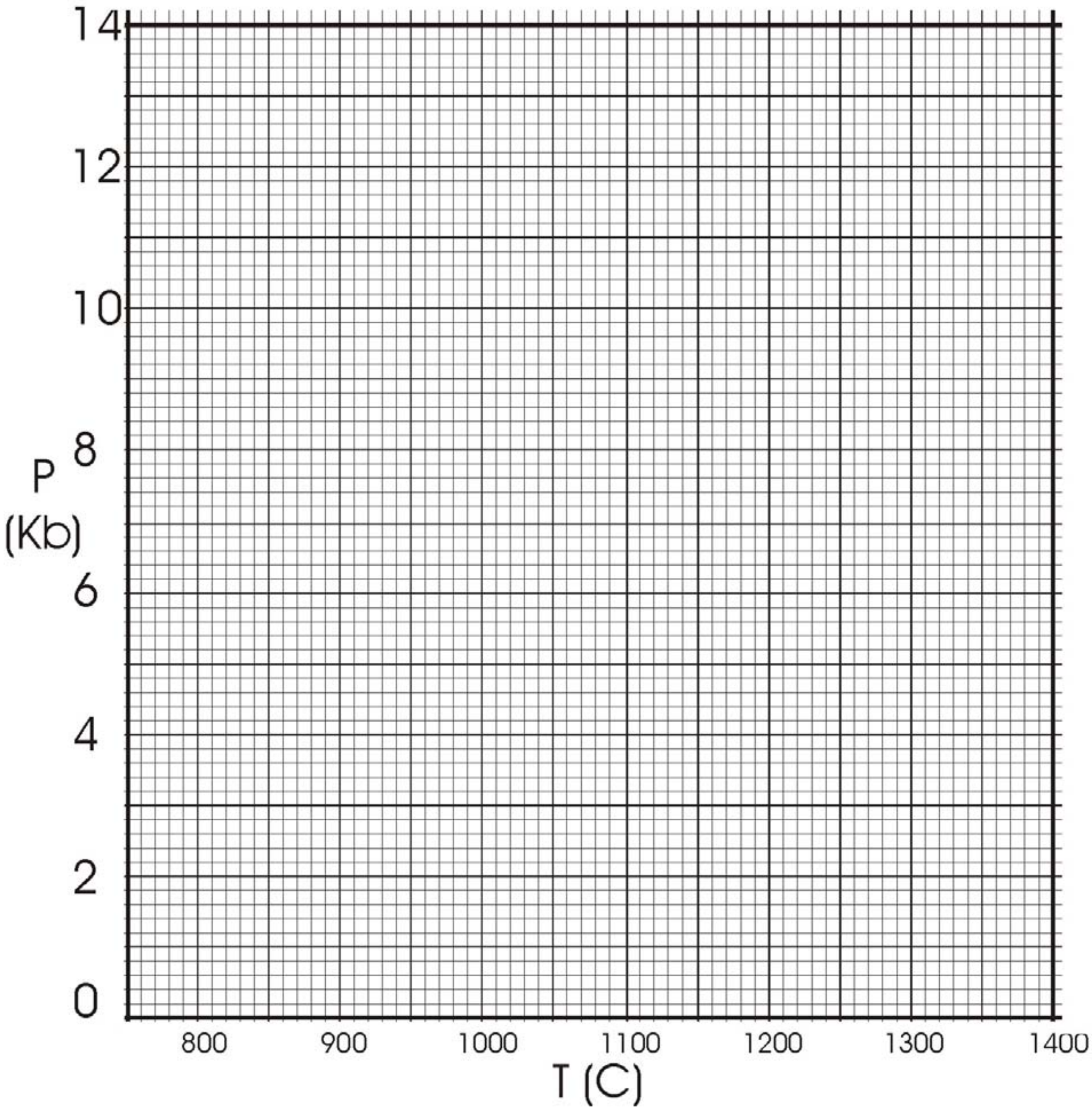
Handy-dandy conversions to remember:
1 joule = 1 J = 10 cm^3-bar = 10 cc-bar

You must use Kelvin for temperature in your calculations but we plot using centigrade. °K = °C + 273.15

You have already calculated)E,)V, and)S for the reaction. Plug the values into the above equation and you will get the equation of a line in P-T space. Be sure to use the correct units (see box).

Note that the Clausius Claperyon equation says the slope of the line dP/dT =)S/)V.

Plot your calculated position for the reaction on the phase diagram below.



While in grad school, Perkins did some experiments on the stability of Gr, Wo, Q and An. He mixed up mixtures of all four minerals and reacted them at different pressures and temperatures. Results are given in the box. Plot these results on your phase diagram (previous page).

Do your thermodynamic calculations agree with Perkins' experiments? If there are discrepancies, hypothesize why they exist.

P	**T**	**results**
1 atm	882	Gr + Q increased
1 atm	910	Gr + Q decreased
4 Kbar	1021	Gr + Q increased
4 Kbar	1042	An + Wo increased
8 Kbar	1164	An + Wo gone
8 Kbar	1174	An + Wo grew
12 Kbar	1296	Gr + Q grew
12 Kbar	1303	Gr + Q gone

The System CaO-Al_2O_3-SiO_2-H_2O

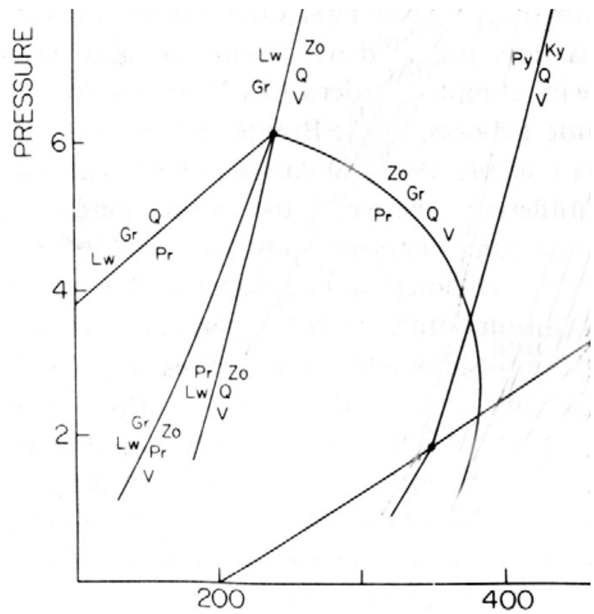
Let's consider the chemical system Ca-Al-Si-H-O = CaO-Al_2O_3-SiO_2-H_2O. This system has five elements, but only four *chemical components* (C=4). Possible minerals include:

mineral	abbreviation	formula
corundum	Co	Al_2O_3
andalusite	And	
sillimanite (these three are polymorphs)	Sill	Al_2SiO_5
kyanite	Ky	
pyrophyllite (a white mica related to talc)	Py	$Al_2Si_4O_{10}(OH)_2$
prehnite (related in some ways to zeolites)	Pr	$Ca_2Al_2Si_3O_{10}(OH)_2$
zoisite	Zo	$Ca_2Al_3(SiO_4)_3(OH)$
gehlenite	Ge	$Ca_2Al_2SiO_7$
grossular (a garnet)	Gr	$Ca_3Al_2Si_3O_{12}$
margarite (a calcic mica)	Mg	$CaAl_2(Al_2Si_2O_{10)}(OH)_2$
lawsonite	Lw	$CaAl_2Si_2O_7(OH)_2$•$3H_2O$
anorthite (a feldspar)	An	$CaAl_2Si_2O_8$
wollastonite (a pyroxenoid)	Wo	$CaSiO_3$
diaspore (a bauxite mineral)	Di	$AlO(OH)$
water (not a mineral, but it can be present)	V	H_2O
quartz	Q	SiO_2

So, if we have a rock that is composed of CaO+Al_2O_3+SiO_2+H_2O, there are many possible minerals. What determines which of the minerals are present?

For example, consider a rock that has a composition equivalent to 100% $CaAl_2Si_2O_8$. It could contain anorthite or it could contain grossular + kyanite + quartz. Write and balance a reaction between anorthite and the other three phases.

How can we determine whether a rock will contain An or Gr+Ky+Q ? What are the controlling factors?



This is a *phase diagram* (pressure vertical, temperature horizontal) showing several reactions . According to this diagram, two reactions limit the stability of prehnite. What are those two reactions? Write them out and balance them. (It might be best to work this out on a separate sheet of paper and just put the answer here.)

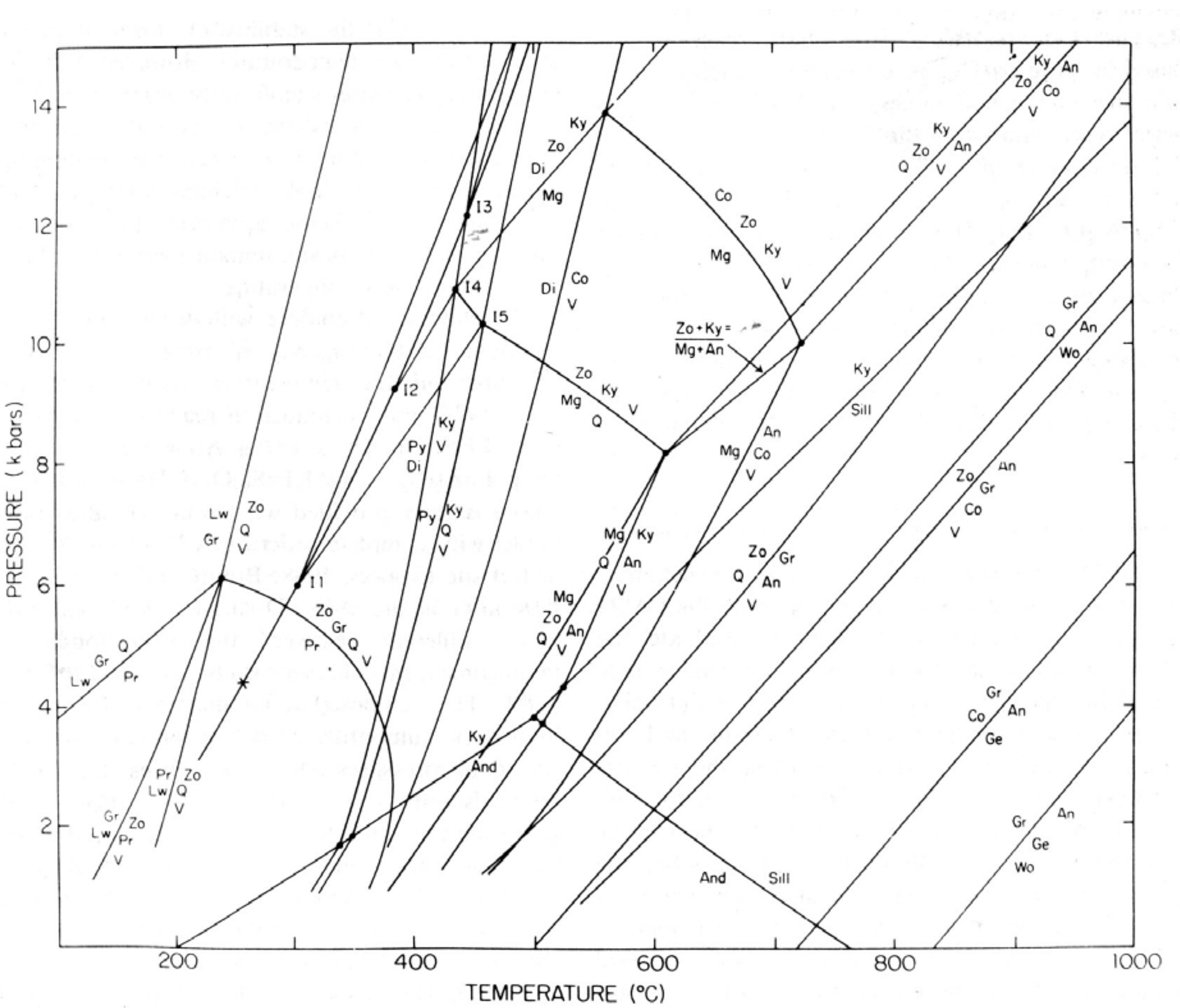
Prehnite (Pr) is only stable below the two limiting reactions. Above the reaction line, prehnite is *unstable* and will break down to Lw+Gr+Q, or to Zo+Gr+Q+V. Why is prehnite less stable than the other minerals at high pressure? (i.e., what properties explain this?)

For one reaction, prehnite is on the low temperature side. For the other, it is on the high temperature side. Why? Explain. (Relate this observation to thermodynamics.)

The *Phase Rule* says that C+2 = P+F. C is the number of *components*. P is the number of *phases* (number of minerals or water) and F stands for the *degrees of freedom*. The reactions that limit prehnite's stability have one degree of freedom (F=1). They are called *univariant reactions*. Along the *univariant reaction lines*, the phases on both sides of the reaction are stable together–nowhere else. An open space on the diagram has F=2, and a specific pressure-temperature (P-T) point (called an *invariant point*) where reactions intersect has F=0.

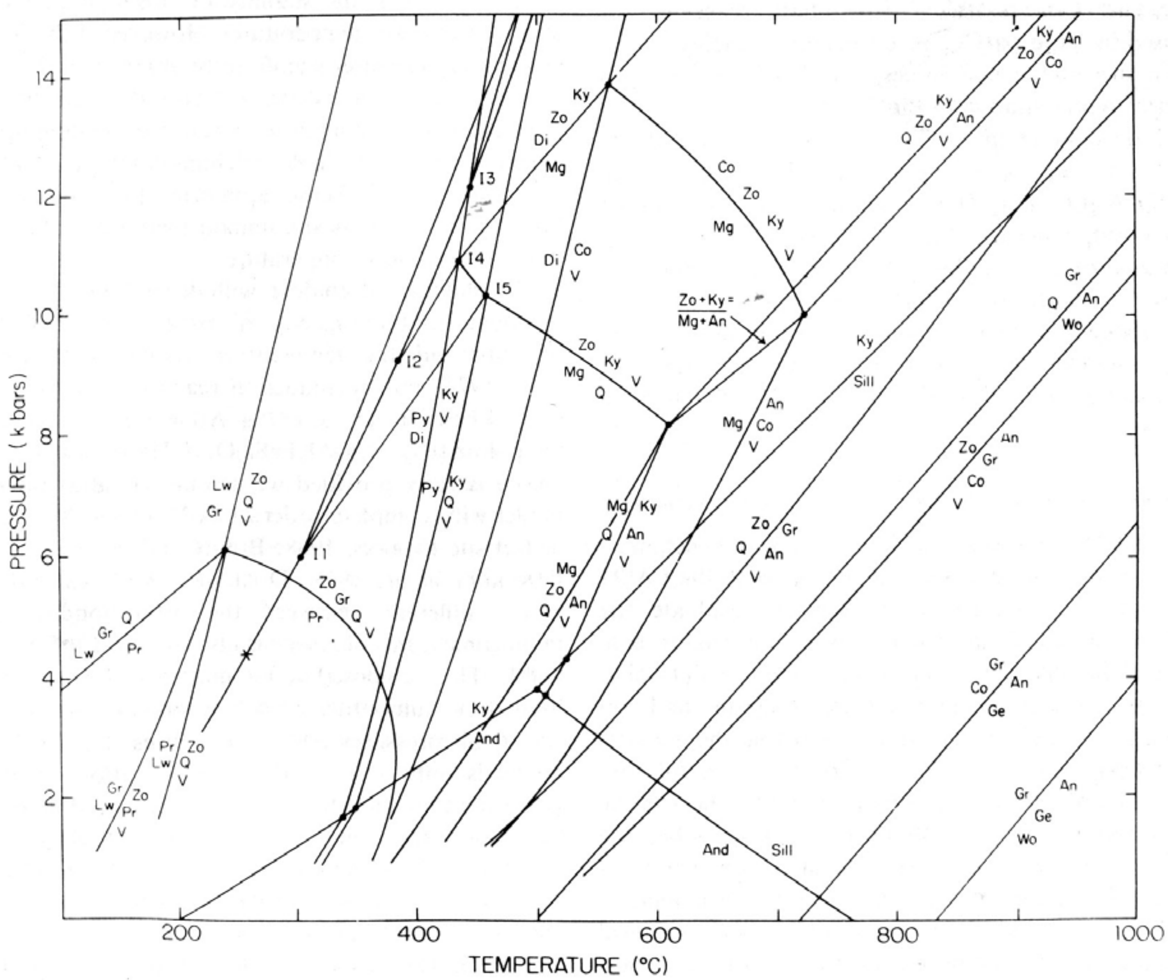
Use the Phase Rule to fill out this chart but putting in the P (number of phases) values in each box:

	F	C=1	C=2	C=3	C=4
space	2				
line	1				
point	0				



Consider the diagram above. It depicts reactions involving minerals in the CaO-Al_2O_3-SiO_2-H_2O system. Some reactions are unlabeled to avoid clutter. And you can ignore the points labeled I1, I2, I3, etc. Note that the reactions divide P-T space into different *divariant fields* (called divariant because P and T can both be changed without leaving the field) where different minerals and different mineral assemblages are stable. For example, andalusite is only stable in a triangular area at the bottom center. Make sure you understand how to interpret these sorts of diagrams.

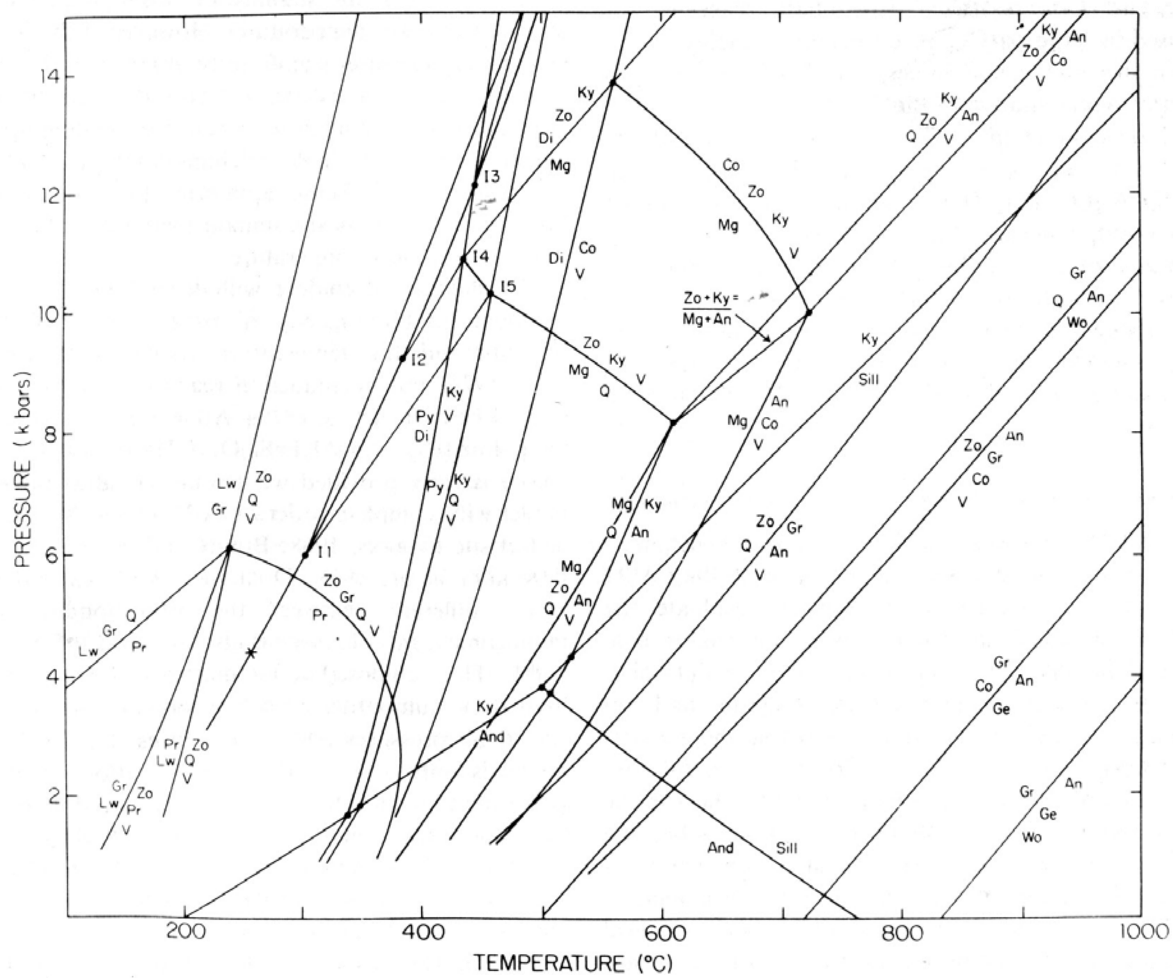
Key point ==> Note, for example that lawsonite (Lw) is stable over the entire diagram, even though some assemblages that contain lawsonite are not. The assemblage Lw+Gr, for example, can only be found on the far left side (below about 200-300 °C), and Lw+Gr+Q is even more restricted.



Where on this diagram is sillimanite stable? (Use arrows or shading if you wish.)

Where on this diagram are grossular + quartz stable?

Where on this diagram is quartz stable?



Where on this diagram is the assemblage kyanite + water(V) stable? (This is tricky!)Where on this diagram are kyanite and sillimanite stable together?

Where on this diagram are prehnite, lawsonite and grossular stable together?

Where on this diagram are zoisite, anorthite and wollastonite stable together?

Where on the diagram are grossular+lawsonite+sillimanite stable together? (Tricky!)

Note that on the previous phase diagram, some reactions have 2 phases in them, some have more, and the most phases in a reaction is 5. Write and balance three reactions (each with a different number of phases in them). Are these consistent with the phase rule? Explain why or why not.